

THE EFFECTS OF HYDROTHERMAL PRETREATMENT ON THE LIQUEFACTION OF COAL.

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Keywords: pretreatment, hydrothermal, coal liquefaction

INTRODUCTION

The effects of aqueous pretreatment on coal and the benefits that can develop for liquefaction or mild gasification are areas of current interest. Most of the work has been conducted with water vapor, and current accounts include that of Bienkowski et al., who found that water vapor pretreatment enhanced liquefaction.¹ Brandes and Graf, reported that treatment of a bituminous coal treated in water vapor at 320°-360°C increased the yields of condensibles in subsequent mild pyrolysis, and they found further that the coal swelled to nearly twice its original volume with the pretreatment.^{2,3} More recent pyrolysis work by Kahn et al. showed that pretreatment with water vapor at 300°-320°C reduced the total oxygen content of low rank coals, but not of high rank coals.⁴

Our work has focused on the use of *liquid* water at elevated temperatures, both as a probe into coal structure,⁵ and as a pretreatment for coal liquefaction. In the work summarized here, we examined the effects of hydrothermal pretreatment at 250°C on conversion of Illinois No. 6 coal (PSOC 1098, and Argonne Premium Coal Bank samples) in tetralin. Related to the effects on conversions are the changes in the pyrolytic behavior of the coal, and some of those results in that area are discussed as well.

RESULTS

Conversion Products

The pretreatments were conducted in small bomb reactors in liquid water at 250°C (~38 atm). The subsequent liquefactions were conducted in stirred autoclaves at 400°C/20 min in tetralin and 500 psi H₂ (cold). The work included studies of both the toluene-soluble (TS) and toluene-insoluble (TI) product fractions, and studies of the pretreated coal itself. All manipulations following the pretreatment were conducted with a minimum of exposure of the product coal to the atmosphere.

Some results are shown in Table 1. The pretreated material was only superficially dried to avoid the risk of altering the material through excessive drying, and some control runs therefore included conversions run with added water (referred to as "wet" tetralin runs below). The table shows that there is little obvious change in the conversions levels, even after a 5 hr pretreatment. Further the elemental analyses in Table 2 show that there is no significant difference in the overall compositions of the TS fractions.

Nonetheless we found the products from the donor conversions of the coal and pretreated coal to be qualitatively different. For example, there is a difference in physical appearance, with the former yielding a brittle solid, and the latter a tacky tar-like product. In accord with this difference differential scanning calorimetry showed the glass transition temperatures to be respectively -20°C and +30°C.

The differences are demonstrated more directly in the data presented in Figure 1 which compares the volatilities and number average molecular weights (M_n) of the TS fractions from conversions of the pretreated and untreated material. The data were obtained with SRI's field ionization mass spectrometer (FIMS) in which the toluene-soluble fractions, fully volatile under these conditions, were evaporated into the instrument over temperatures from ambient to 500°C at a heating rate of 2.5°C/min. The data in Figure 1(a) show that the TS fraction from the pretreated coal were significantly more volatile than that from the untreated material. The temperatures at half volatility were 205°C and 250°C for the pretreated and unpretreated cases, respectively.

The M_n values of the products ranged monotonically from 150-200 amu for the most volatile portions to 750 amu for the least volatile for both products, but with some prominent differences as shown in Figure 1(b). The figure shows a breakdown of M_n over temperature intervals in terms of the difference $M_n[\text{pretreated}] - M_n[\text{wet tetralin}]$, and substantial M_n differences are concentrated in the more volatile half. Thus ΔM_n grows to just above 100 amu up to about 200°C, while the M_n 's for the less volatile half of the products are similar.

Pretreated Coal

Elemental Analyses and Morphology. These changes suggested considerable differences in the pretreated coal, and we accordingly conducted a series of comparisons between it and the as-received material. The elemental and ash analyses are presented in Figure 2, with the O-values were obtained by direct O-analysis. The figure shows that the H/C and O/C ratios changed only slightly. However the, bulk sulfur content was substantially reduced by about 60%, and matched by lowered ash levels. The similarity demonstrates that ash reduction by the hydrothermal medium must involve removal primarily of sulfur-containing material, most likely sulfate.

These results are qualitatively similar to those of Rozgonyi et al.,⁶ who reported 39% and 31% reductions, respectively, in total sulfur and ash for a bituminous coal after hydrothermal treatment at 292°C/40 min. Our higher values may be due to our lower temperature, which should minimize thermal degradation of the organic portion of the coal.

Pyrite is fully insoluble in water at these conditions, and these results are likely related to the ease with which coal pyrite is oxidized to sulfate, which would then be water soluble. It is reported for example that greater than 98% of the pyritic sulfur in a fresh sample of Illinois No. 6 coal stored in an evacuated desiccator was oxidized to ferrous and ferric sulfate over a year.⁷ The material was exposed to the atmosphere for only short intervals over that period for sampling, and yet the mineral sulfur oxidation was virtually complete.

It is noted in geochemical studies of marine sediment maturation that aqueous iron sulfate at hydrothermal conditions oxidizes organic material.^{8a} This factor could play a key role in the pretreatment effect, since the sulfate in coal would be very finely dispersed. Indeed in scanning electron microscope (SEM) and energy dispersive X-ray (EDX) studies we found iron to be very broadly and evenly distributed throughout the organic phase of the coal. It could therefore be responsible for oxidatively breaking critical linking groups in the crosslinked matrix. Another explanation could be tied to the observation that in the oxidation process the sulfate is reduced to products containing pyrrhotite,^{8b} and pyrrhotite has in turn been associated with the benefits to liquefaction produced by the H_2S/Fe_xS_y family.^{8c} Thus oxidation of small quantities of organic material could result in relatively large quantities of very highly dispersed pyrrhotite, positively affecting the conversions.*

The morphological changes brought about by the pretreatment were demonstrated by further SEM/EDX work. We found the starting coal to be present in particles of nominally 50-200 μm , with separate particles representing both the bulk organic and bulk mineral phases. The hydrothermal treatment, however, substantially decreased the particle size of the coal, with the formation of a fines fraction with nominal particle sizes below 1 μm . A profound change occurred in the bulk mineral phase, which became fragmented and irregular in appearance.

As for Fe, we saw considerable quantities of Al and Si in the organic phase, an observation in line with the split of the mineral components in coal between the bulk organic and mineral phases discussed by Finkelman.⁹ Allen and VanderSande¹⁰ have estimated that mineral matter in the organic phase may represent up to 15% of the total quantity of mineral material in coal. A distribution of such a fine mineral material throughout the organic phase would lead to a significant interfacial volume, and could be responsible for the effects of hydrothermal pretreatment. This view is in line with suggestions by Mraw et al.,¹¹ that mineral material within the organic phase could be significant to the behavior of coal in general.

Coal Pyrolysis, Volatility, and Volatile Products. The effects of pretreatment on volatility properties were studied by FIMS, comparing the volatiles from both the as-received coal and the hydrothermally pretreated material. The samples were heated slowly in the inlet from ambient to 500°C, and the signal was recorded throughout the heating period. The total volatile yields were virtually identical, 22% and 23% of the as-received and pretreated samples, respectively; however, as shown in Figure 3, the two

* Pyrrhotite would be formed in the conversion step anyway. However its formation at lower temperatures in the pretreatment step would maintain the fine dispersal, and benefit the subsequent conversion.

samples behaved very differently. The figure shows the \bar{M}_n of evolving material plotted against temperature. The profile for the as-received coal steadily increases to a single maximum with increasing temperature, a behavior expected from the thermolysis of a highly crosslinked material. The profile for the pretreated material, on the other hand, is clearly different. It appears to be the sum of profiles for the as-received coal and for a second, more volatile quantity of condensibles produced by the pretreatment, a view consistent with the fact that the number average molecular weight of the volatiles is reduced from 347 amu for the tar from the as-received material to 326 amu for the pretreated coal tar.

Additional FIMS data are shown in Figure 4, which shows the differences in the distribution of molecular weights in the pretreated and as-received samples. Specifically the figure plots the response difference, (pretreated) - (as-received), against molecular weight intervals up to 750 amu. The figure demonstrates a broad enrichment in lower molecular weight material at the expense of higher weight tars. Thus the behavior is not merely a release of trapped material. Rather, the results suggest that the treatment changes the coal in some manner such that the tar precursors generate additional lower weight material.

This absolute increase in lighter material is demonstrated by yet other FIMS data in Figure 5. The figure shows the thermal evolution profiles for benzene, naphthalene the arenes and their corresponding methyl, dimethyl and trimethyl derivatives.* The figure shows that they evolve distinctly differently after pretreatment, distilling from the matrix at considerably lower temperatures.

DISCUSSION

Our results demonstrate that coal contains regions with structural components significantly reactive under the hydrothermal environment. While the specific mechanism for this process remains to be developed, this activity is reminiscent of findings in studies of accelerated maturation of oil shale, where hydrothermal treatment (hydrous pyrolysis) leads to the production of petroleum hydrocarbons.¹²

Recent results by Hoering¹³ are particularly applicable to the present case. In that work the treatment of preextracted Messel shale with water at 330°C/3 days generated petroleum hydrocarbons including long chain normal alkanes, aromatics, and biomarkers. When D₂O was used, deuterium was heavily incorporated into the hydrocarbons. The control results and the distributions of isotopic isomers rule out virtually all sources for the hydrocarbons and exchange except chemistry at the preexisting-interphase layer at the mineral/kerogen boundary.[†] Thus the mineral component of the oil shale, or more specifically the interfacial volume joining the kerogen and mineral phases, must play a significant role in the process.

When viewed in that context, the pretreatment-generated hydrocarbons for coal case reflects the presence of similar immature regions. Such regions have not been included in the coal structures commonly presented, and the possibility of their existence emphasizes the need to consider an the mineral phase in coal as a key part of the structure. It is likely these regions are significant not only under hydrothermal conditions, but reactive in a more general sense and significant to the chemistry of coal at reducing/conversion conditions. Thus the conversions of the less mature, lower rank coals could particularly benefit from hydrothermal pretreatment in terms of both product quality and quantity.

ACKNOWLEDGEMENT

We acknowledge the support of this work on DOE Contract No. DE-FG22-87PC79936.

* The FIMS mass values can correspond in some cases to several different structures. However given the relatively low molecular weights here, it is likely that the assignments are primarily as assigned. An exception is the case for the naphthalenes, which have the same molecular weights as the family of alkanes.

† Unextracted alkanes or alkenes were as sources were eliminated in controls with extracted shale spiked with an n-alkane or terminal n-alkene. The alkane was recovered unexchanged, and 60% of the olefin was recovered as the corresponding alkane, and only slightly tagged. Thermally generated radicals from the kerogen could also be dismissed. Organic radicals at these conditions should react only very slowly with D₂O on thermochemical grounds. Moreover any resulting deuterated hydrocarbons would have an isotope distribution far too narrow to match the observed, broad distributions.

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Table 1
EFFECT OF PRETREATMENT ON CONVERSIONS OF ILLINOIS
NO. 6 COAL TO TOLUENE-SOLUBLE PRODUCTS^a

	Pretreatment ^b	%TS (daf)
<u>PSOC 1098</u>		
	none	48
		47
	none	49
	(water/tetralin) ^c	48
	H ₂ O (30 min)	52
		50
	H ₂ O (5 hr)	49
<u>Argonne Premium Sample</u>		
	none	59
	none	56
	(water/tetralin) ^c	

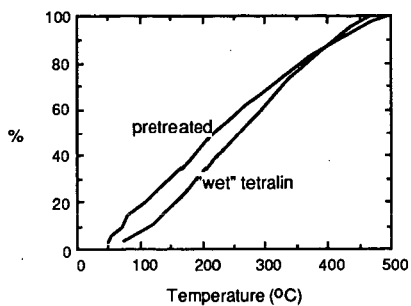
^a Reaction conducted in 300-ml autoclave with 5 g coal in 30 g tetralin and 500 psi H₂(cold) at 400°C/20 min

^b Coal (5 g) was pretreated with 10 ml H₂O at 250°C and 500 psi N₂ (cold) in a 45 ml Parr reactor.

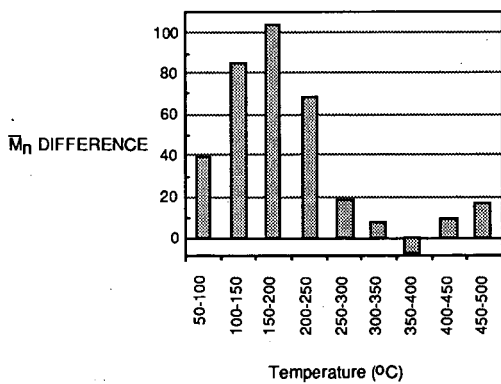
^c 4 ml water added to tetralin in the conversion of as-received coal.

Table 2
Elemental Analyses of Products from Tetralin Conversions of
Illinois No. 6 Coal at 400°C/20 Min

Condition		H/C	%O (diff)	%S	%N
Dry Tetralin	TS	0.98	5.0	1.1	1.2
	TI	0.77	-	-	1.9
Wet Tetralin	TS	0.98	5.0	1.0	1.4
	TI	0.81	-	-	2.0
Pretreated	TS	1.02	4.7	0.9	0.9
	TI	0.73	-	-	2.0



(a) Fraction of total volatility versus evaporation temperature.



(b) Difference number average molecular weight (pretreated - wet tetralin) versus temperature.

Figure 1. Comparison of toluene-soluble fractions from conversions of pretreated and as-received coal.

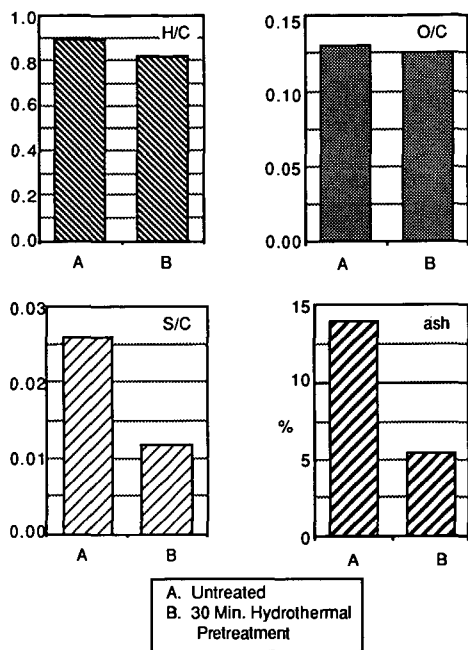


Figure 2. Analytical data for untreated and hydrothermally pretreated Illinois No. 6 coal.

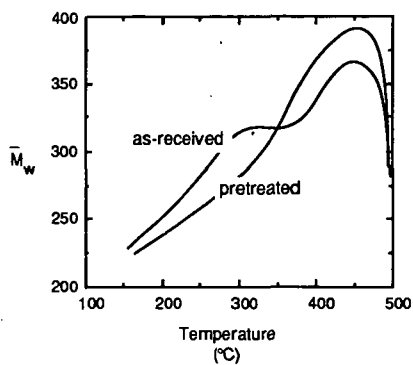


Figure 3. FIMS analysis of pretreated and as-received Illinois No. 6 coal.

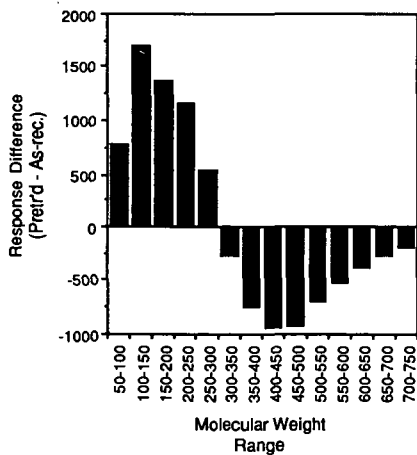


Figure 4. FIMS response differences as a function of molecular weight range. The response data have been normalized so that the values from the two materials can be directly compared.

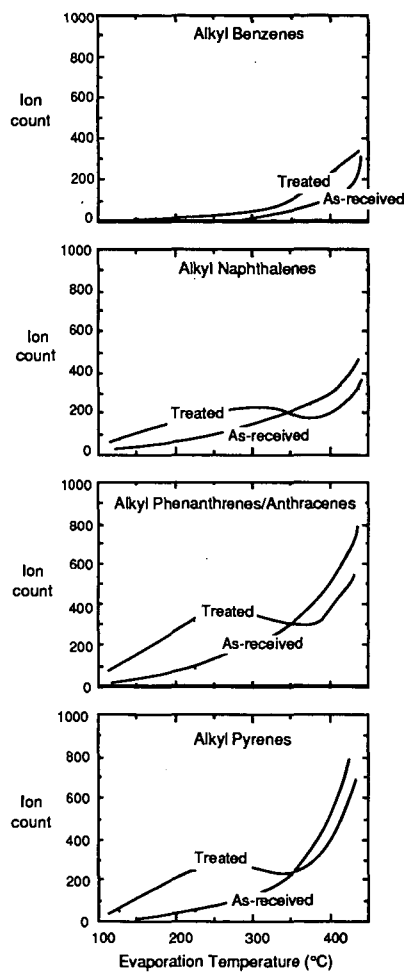


Figure 5. Thermal generation of arenes under hydrothermal conditions. The abscissa values refer to the FIMS sample holder temperature.